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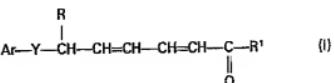
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(54) 2,4-Hexadienoic acid derivatives useful as weed-killers and phytogrowth regulators

(57) Novel 2,4-hexadienoic acid derivatives of the general formula:



in which:

R represents a hydrogen atom or a methyl group,

Y represents an oxygen atom or a divalent sulphur atom,

R' represents OR², SR² or N(R¹)₂, in which R¹ represents a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, a cycloalkyl group having 3 to 6 carbon atoms, an alkenyl group having 2 to 4 carbon atoms, an alkyne group having 2 to 4 carbon atoms, a phenyl group or a benzyl group,

Ar represents a phenyl, pyridyl, naphthyl, quinoline, phenoxy-phenyl or pyridyloxy-phenyl group, any of which groups may be substituted by one or more substituents selected from halogen atoms, alkyl groups having 1 to 4 carbon atoms, alkoxy groups having 1 to 4 carbon atoms, nitro, cyano, trifluoromethyl, acetoxy, acetamido and methoxycarbonyl groups are endowed with weed-killing and phytogrowth regulating activity.

GB 2 101 600 A

SPECIFICATION

2,4-Hexadienoic acid derivatives useful as weed-killers and phytogrowth regulators

This invention relates to hexadienoates and to their preparation and in particular to 2,4-hexadienoic acid derivatives mono or disubstituted in the 6-position which are endowed with weed-killing and phytogrowth regulating activities. The invention also relates to the use of such compounds in the protection of agrarian cultivations from the infesting plants and to the utilisation thereof as phytogrowth regulators.

One of the weed-killers commonly used in agriculture is 2,4-dichloro-phenoxyacetic acid (commercial name: 2,4 D), the herbicide activity of which was first disclosed by P.W. Zimmerman and 10 A. E. Hitchcock in Contr. Boyce Thompson Inst., 12, 321 (1942). This compound possesses excellent herbicide properties especially in the post-emergence treatments.

However, 2,4 D is a highly volatile compound, and this feature represents a serious disadvantage because, both during application and after, the compound can be transferred to adjacent cultivations, damaging them irretrievably. Furthermore, the widespread use of 2,4 D has facilitated the development 15 of infesting plants capable of withstanding its weed-killing activity.

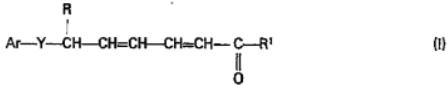
In an attempt to overcome these disadvantages, a large number of chemical compounds have been synthesised the structures of which are derived either directly or indirectly, from that of 2,4-dichloro-phenoxyacetic acid.

For example, Belgian Patent Specification No. 774,748 discloses naphthoxy-acetic derivatives, 20 Belgian Patent Specification No. 864,632 discloses phenoxy-phenoxyacetic derivatives and Belgian Patent Specification No. 871,523 discloses phenoxy-phenoxyacetonitrile derivatives.

2,4-dichloro-phenoxyacetic acid is also endowed with a phytotoxicity prevents it from being utilised as a phytogrowth regulator.

We have now found that some of the 2,4-hexadienoic acid derivatives are endowed both with a 25 weed-killing activity with a high selectivity towards important agrarian cultures and with a phytogrowth regulating activity.

Therefore according to the present invention there is provided a compound of the general formula:



in which:

30 R represents a hydrogen atom or a methyl group,
Y represents an oxygen atom or a divalent sulphur atom,
R' represents OR², SR² or NR²R₃, in which R² represents a hydrogen atom, an alkyl group having 1

to 4 carbon atoms, a cycloalkyl group having 3 to 6 carbon atoms, an alkenyl group having 2 to 4 carbon atoms, an alkynyl group having 2 to 4 carbon atoms, a phenyl group or a benzyl group,

35 Ar represents a phenyl, pyridyl, naphthyl, quinoline, phenoxy-phenyl or a pyridyloxyl-phenyl group, any of which groups may be substituted by one or more substituents selected from halogen atoms, alkyl groups having 1 to 4 carbon atoms, alkoxy groups having 1 to 4 carbon atoms, nitro, cyano, trifluoromethyl, acetoxy, acetamido and methoxycarbonyl groups.

The compounds of general formula (I) are endowed with weed-killing (herbicide) and phytogrowth 40 regulating activities and may be advantageously employed in agriculture.

The preparation thereof is carried out according to techniques which are commonly used in the organic chemistry practice.

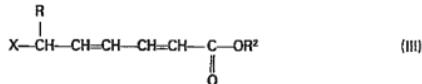
A versatile synthesis consists in condensing an alkaline salt of the formula:



45 in which:

M[⊕] represents the cation of an alkaline metal, and

Ar and Y are as defined above,
with an alkyl ester of the formula:



in which:

R^2 represents a lower alkyl having 1 to 4 carbon atoms,

R represents a hydrogen atom or a methyl group, and

X represents a chlorine, bromine or iodine atom.

- 5 This reaction yields compounds of formula (I), in which R^1 is a group OR^2 , and R^2 is an alkyl group (ester derivatives). 5

The other compounds of formula (I) may be prepared from these compounds, by operating according to conventional techniques. For example, by hydrolysis it is possible to prepare the carboxylic acids ($R = OH$), which can be converted into the corresponding acyl halides and reacted with suitable 10 alcohols, thiols or amines, thus obtaining the compounds of formula (I) in which $R^1 = OR^2$, SR^2 and $N(R^2)_2$, respectively. 10

The condensation between salt (III) and ester (III') is generally conducted in an inert gas atmosphere and in a polar solvent. After stirring for a few hours at a temperature ranging from room temperature to the solvent boiling temperature, the reaction is completed and the product is isolated according to the 15 conventional laboratory techniques. 15

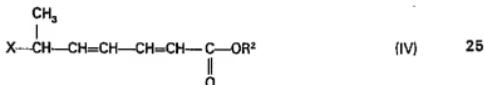
The compounds of formula (I) are in the form of solids or liquids having a high boiling point.

The alkaline salts of formula (III) are compounds generally known or readily prepared from known compounds according to conventional techniques.

Also the compounds of formula (III'), in which $R = H$, are known compounds and may be obtained, 20 for example, by the methods described in Helvetica Chimica Acta 29, 1191 (1946), or in Journal of the Chemical Society, page 866 (1946).

The compounds of formula (III'), in which $R = CH_3$, are believed to be new compounds.

Therefore according to a further aspect of the present invention, there is provided compounds of the formula:

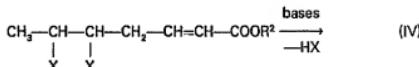
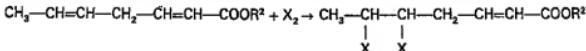


In which:

X represents a chlorine, bromine or iodine atom, and

R^2 represents an alkyl group of 1 to 4 carbon atoms.

Such compounds are prepared by halogenation and dehydro-halogenation of alkyl 2,5-30 heptadienoate, which is a known compound, according to the following reactions: 30



The preparation of a compound of formula (IV) is described in Example 1.

The compounds of formula (I) are endowed with a high weed-killing activity. Within the broad class 35 thereof, some compounds exhibit a more effective action against the dicotyledonous weeds, others against the monocotyledonous weeds, retaining in every case a high selectivity towards useful cultures. Furthermore the compounds are active both during the pre-emergence (i.e. when the infesting plant has not yet emerged from the earth) and during the post-emergence. Optimum results are obtained from the use during the post-emergence period.

40 As regards the weed-killing activity, the preferred compounds are those of formula (I), in which R is a hydrogen atom and Ar is a substituted phenyl, or R is a methyl group and Ar is a phenoxy-phenyl group or an optionally substituted pyridinoxy-phenyl group.

For the practical uses in agriculture, the compounds of formula (I) may be used as such or in the form of formulations. Such formulations may include, in addition to one or more of the compounds of 45 formula (I) as active substance, solid or liquid vehicles and, optionally, surfactants, emulsifiers and other additives. If desired, it is possible to include other compatible active substances e.g. fertilizers, phytopharmaceutical regulators and other weedkillers.

The herbicide compositions can be formulated, according to the conventional agricultural techniques, in granules, powders, wettable powders, emulsifiable concentrates and the like. Depending on the type of composition and on the specific use it is intended for, the active substance may be

contained in amounts varying from 1 to 99% by weight.

The amount of composition or formulation to be distributed in the area to be protected against the weeds varies as a function of different factors such as the type of composition of formulation and respective effectiveness of the particular active substance contained therein, the kind of infestation and 5 its degree, the type of cultivation, climatic and environmental factors. In general, the amount of active substance to be distributed in order to get a satisfactory protection of the cultures against the weeds, ranges from 0.3 to 6 kg/ha.

The compounds of general formula (I) possess, additionally, interesting phytogrowth regulating properties in various fields of application. For example, they promote the setting of the flowers, that is 10 the development of parthenocarpic fruits without any pollination having occurred. Such capability is generally utilized to promote the setting in greenhouse cultivations of tomato and pepper. Another utilization of the phytogrowth regulators is that of stimulating the root growth in the scions.

A further utilization for which the compounds of formula (I) are suitable is that of reducing the fruit drop prior to harvesting, with particular regard to apple trees.

15 The phytogrowth regulating action exerted by the compounds of formula (I) may vary in degree as a function of the compound and of the kind of action required. However, in the range of the class, several compounds have proved to possess a phytogrowth regulating activity comparable with the one of the commercially available phytogrowth regulators of different chemical classes, and a few compounds have proved to be even better than the specific commercial compounds intended for that 20 particular type of utilization.

In the practical application as phytogrowth regulators, the compounds of formula (I) may be used in the form of emulsifiable concentrates, other formulations being of little interest from a practical viewpoint, owing to the particular use.

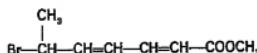
25 The emulsifiable concentrates contain, in addition to one or more compounds of formula (I) as active substance, suitable solvents and surfactants. A certain amount of water may be still present in the concentrates.

When carrying out the treatment, the concentrate is diluted in water to obtain the desired concentration of active substance which, for the setting treatment, is generally from 10 to 200 mg/l, preferably around 100 mg/l, while for the fruit drop-preventing treatment the concentration is generally 30 from 1 to 10 g/l, preferably about 3 g/l.

The invention will now be illustrated by the following Examples.

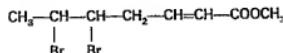
EXAMPLE 1

Preparation of methyl 6-bromo-hepta-2,4-dienoate



35 A solution containing 50.9 g (0.318 moles) bromine in 100 ml of CCl_4 was added dropwise over about 2 hours to a solution containing 44.6 g (0.318 moles) methyl 2,5-heptadienoate [prepared according to G.B. Chiusoli — La Chimica e l'Industria (The Chemistry and the Industry) 41, 506 (1959)] in 50 ml of CCl_4 maintained under stirring at -15°C . On completion of the addition, the temperature was allowed to rise spontaneously to room temperature.

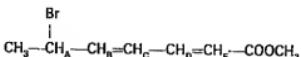
40 The reaction mixture was then distilled under vacuum and the fraction which boiled at 100 to 105°C at a pressure of 0.1 mm Hg was collected to yield 65.72 g of methyl 5,6-di-bromo-hept-2-enoate of the formula:



45 63.4 g (0.21 moles) of this ester were dissolved in 200 ml of methylethylketone, and 29 g (0.21 moles) of anhydrous potassium carbonate were added to the solution. The reaction mixture was then heated under reflux for about 30 hours. The solvent was then cold removed by evaporation at reduced pressure. The crude product was diluted with ethyl ether and washed with water until a neutral pH was obtained.

The ethereal solution was then dried and the solvent was removed by evaporation at reduced 50 pressure. The crude product was then distilled under high vacuum, and the fraction boiling at 80°C at a pressure of 0.1 mm Hg was collected to yield 26.9 g of the desired product (elemental analysis and IR analysis were consistent with the assigned structure).

¹H NMR (CDCl₃, TMS)



δ (ppm): 1.82 (d, 3H, CH₃—CH)

3.76 (s, 3H, COOCH₃)

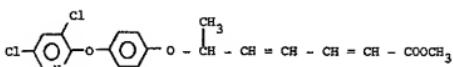
- 5 4.77 (m, 1H, H_A)
 5.7—6.8 (m, 3H, H_B + H_C + H_D)
 7.0—7.7 (m, 1H, H_E)

[s = singlet, d = doublet, m = multiplet].

EXAMPLE 2

- 10 Preparation of methyl 6-(3',5'-dichloro-2'-pyridinoxy-phenoxy-hepta-2,4-dienoate

10



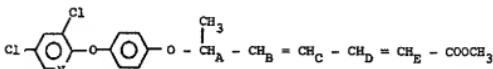
3.2 g (0.0125 moles) of sodium 4-(3',5'-dichloro-2'-pyridinoxy)-phenate, 3.2 g (0.0146 moles) of methyl 6-bromo-2,4-heptadienoate and 10 cc of methanol were introduced into a 100 cc flask equipped with a magnetic stirrer and maintained in a nitrogen atmosphere. The reaction mixture was 15 stirred for 2 hours at a temperature of 0°C.

The methanol was evaporated at room temperature and the residue was diluted with ethyl ether. The ethereal solution was washed with dilute aqueous soda and successively with water till a neutral pH was obtained.

Upon evaporation of the solvent, 3.4 g of the desired product, which was re-crystallised from 20 petroleum ether (melting point = 100 to 103°).

20

¹H NMR (CDCl₃, TMS)



δ (ppm): 1.45 (d, 3H, CH—CH₃)

3.72 (s, 3H, COOCH₃)

- 25 4.85 (m, 1H, H)
 5.64—6.62 (m, 3H, H_C + H_D + H_E)
 6.7—8 (m, 7H, aromatic protons + H_B)

25

[s = singlet, d = doublet, m = multiplet].

EXAMPLE 3

- 30 Preparation of methyl 6-(3-trifluoromethylphenoxy)-hexa-2,4-dienoate

30



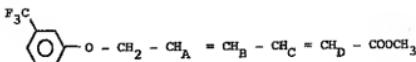
3.6 g (0.02 moles) of sodium 3-trifluoromethylphenate, 4.2 g (0.02 moles) of methyl 6-bromo-hexa-2,4-dienoate, and 50 ml of methanol were introduced into a 100 ml flask equipped with a reflux condenser and a magnetic stirrer and maintained in a nitrogen atmosphere.

- 35 The reaction mixture was stirred in a nitrogen atmosphere for 3 hours at a temperature of 35°C.

The methanol was then evaporated and the residue was diluted with ethyl ether. The ethereal solution was washed with water and dried on anhydrous Na₂SO₄. The solvent was then evaporated and the residue was distilled under high vacuum and the fraction which boiled at 90°C at a pressure of 0.05 mm Hg was collected to yield 3.4 g of the desired product.

35

¹H NMR (CDCl₃, TMS)



- δ (ppm): 3.8 (s, 3H, CH₃)
 4.8 (d, 2H, CH₂)
5 5.9—6.8 (m, 3H, H_B + H_C + H_D)
 7—7.8 (m, 5H, H_A + aromatic protons)

5

[s = singlet, d = doublet, m = multiplet].

EXAMPLE 4

- Compounds of general formula (I) reported in the following Table 1 were prepared by analogous
10 procedures to those described in Example 2 or Example 3. The compounds in which R¹ = OH were
prepared from the corresponding compounds in which R¹ = OCH₃, by hydrolysis according to
conventional techniques.
- 10

Table 1
 Compounds of formula (I) $\text{Ar} - \text{Y} - \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{C} = \text{R}^1$
 R

Compound No.	Ar	Y	R	R ¹	Physical state at room temperature	melting point (mp) (2) boiling point (bp)
1		O	H	OCH ₃	solid	mp 115°C
2		O	H	OCH ₃	solid	mp 67 to 68°C
3		O	H	OCH ₃	solid	mp 61 to 63°C
4		O	H	OCH ₃	solid	mp 72 to 74°C
5		O	H	OCH ₃	solid	mp 100°C

Compounds of formula (IX)

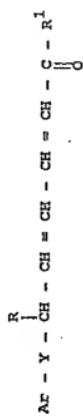


Table I

Compound No.	Ar	Y	R	R'^1	Physical state at room temperature	melting point (mp) boiling point (bp)
6		O	H	OCH_3	solid	mp 100°C
7		O	H	OCH_3	solid	mp 142°C
8 (3)		O	H	OCH_3	liquid	bp 90°C at 0.05 mm Hg
9		O	H	OH	solid	mp 110 to 115°C

Table I
 $\begin{array}{c} \text{R} \\ | \\ \text{Ar} - \text{Y} - \text{CH} = \text{CH} = \text{CH} = \text{CH} - \text{C} = \text{O} - \text{R}' \end{array}$

Compound No.	Ar	Y	R	R'	Physical state at room temperature	melting point (mp) boiling point (bp)
10		O	H	OH	solid	mp 140 to 150°C with decomposition
11		O	H	OCH ₃	solid	mp 75 to 80°C
12		S	H	OCH ₃	liquid	bp 150 to 155°C at 0.1 mm Hg
13		S	H	OCH ₃	liquid	bp 140 to 145°C at 0.1 mm Hg

Compounds of formula (I)

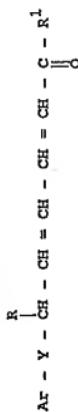


Table I

Compound No.	Ar	Y	R	R ¹	Physical state at room-temperature	melting point (mp) (2) boiling point (bp)
14	$\text{F}_3\text{C}-\text{C}_6\text{H}_4-$	O	H	OCH_3	solid	mp 62 to 64°C
15	C_6H_4-	O	H	OCH_3	solid	mp 74 to 76°C
16	$\text{H}_3\text{C}-\text{O}-\text{C}_6\text{H}_3-\text{C}_6\text{H}_4-$	O	H	OCH_3	solid	mp 100°C
17	$\text{NC}-\text{C}_6\text{H}_4-$	O	H	OCH_3	solid	mp 114°C

Compounds of formula (IX)

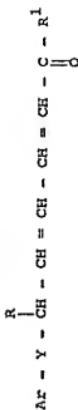


Table I

Compound No.	Ar	Y	R	R'	Physical state at room temperature	Melting point (mp) (2) Boiling point (bp)
18		o	H	OCH ₃	solid	mp 50 to 55°C
19		o	H	OCH ₃	solid	mp 78°C
20		o	H	OCH ₃	solid	mp 55°C
21		o	H	OH	solid	mp 155 to 160°C

Table I
 Compounds of formula (IX) $\text{Ar} - \text{Y} - \underset{\text{R}}{\text{CH}} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \underset{\text{R}^1}{\text{C}} = \text{O}$

Compound No.	Ar	Y	R	R^1	Physical state at room temperature	melting point (mp) (2)	boiling point (bp)
22	$\text{H}_3\text{C}-\text{O}-\text{NH}-\text{C}_6\text{H}_4-$	O	H	OCH_3	solid	mp 155°C	
23	$\text{F}-\text{C}_6\text{H}_4-$	O	H	OCH_3	solid	mp 48 to 52°C	
24	$\text{Cl}-\text{C}_6\text{H}_3(\text{N})-\text{C}_6\text{H}_4-$	O	H	OCH_3	solid	mp 100 to 103°C	
25	$\text{Cl}-\text{C}_6\text{H}_4-\text{Cl}$	O	H	OH	solid	mp 105 to 110°C	

Compounds of formula (I)

$\text{Ar} - \overset{\text{R}}{\underset{\text{O}}{\text{Y}}} - \text{CH} = \text{CH} \approx \text{CH} - \text{CH} \approx \text{CH} - \overset{\text{R}^1}{\underset{\text{O}}{\text{C}}} - \text{R}^1$

Table 1

Compound No.	Ar	Y	R	R^1	Physical state at room temperature	melting point (mp) (2) boiling point (bp)
26		o	H	OCH_3	solid	mp 60 to 65°C
27	$\text{H}_3\text{C}-\overset{\text{NH}}{\underset{\text{O}}{\text{C}}}-\text{Ar}$	o	H	OCH_3	solid	mp 162 to 166°C
28		o	CH_3	OCH_3	liquid (4)	$^1\text{H} - \text{NMR}$ (5) (δ, ppm) 1.52 (d, 3H); 3.84 (s, 3H); 4.97 (m, 1H); 5.9-6.68 (m, 3H); 6.78-7.98 (m, 9H)
29		o	CH_3	OCH_3	liquid (4)	$^1\text{H} - \text{NMR}$ (6, ppm) 1.42 (d, 3H); 2.23 (s, 3H); 3.65 (s, 3H); 4.95 (m, 1H); 5.6-6.3 (m, 3H); 6.5-7.4 (m, 9H)

Compounds of formula (I)



Table I

Compound No.	Ar	Y	R	R ¹	Physical state at room temperature	melting point (mp) (2) boiling point (bp)
30	$\text{F}_3\text{C}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O}-$	o	CH_3	OCH_3	Liquid (4)	1H-NMR (δ , ppm) 1.47 (d, 3H); 3.7 (s, 3H); 4.8 (m, 1H); 5.55-6.42 (m, 3H); 6.58-7.78 (m, 9H)
31	$\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O}-$	o	CH_3	OCH_3	Liquid (4)	1H-NMR (δ , ppm) 1.48 (d, 3H); 3.76 (s, 3H); 4.91 (m, 1H); 5.77-6.66 (m, 3H); 6.77-7.66 (m, 9H)
32	$\text{Cl}-\text{C}_6\text{H}_3(\text{CH}_3)-\text{O}-\text{C}_6\text{H}_4-\text{O}-$	o	CH_3	OCH_3	Liquid (4)	1H-NMR (δ , ppm) 1.42 (d, 3H); 2.2 (s, 3H); 3.68 (s, 3H); 4.76 (m, 1H); 5.64-5.37 (m, 3H); 6.52-7.53 (m, 8H)
33 (6)	$\text{Cl}-\text{C}_6\text{H}_3(\text{Cl})-\text{O}-\text{C}_6\text{H}_4-\text{O}-$	o	CH_3	OCH_3	Solid	mp 100 to 103°C

Notes to Table 1

- (1) Elemental analysis and I.R. and N.M.R. spectroscopic data of each compound are consistent with the assigned structure.
 (2) The melting points recorded on Table 1 were not corrected.
 5 (3) The preparation of Compound No. 8 is described in Example 3.
 (4) This compound decomposes on heating before distillation.
 (5) The ¹H—NMR spectra reported on Table 1 were recorded by using CDCl₃ as a solvent and TMS as internal standard; s = singlet, d = doublet, m = multiplet.
 (6) The preparation of Compound No. 33 is described in Example 2.

10 EXAMPLE 5

10

Determination of the weed-killing activity

Pots (top diameter = 10 cm, height = 10 cm) were prepared containing sandy earth and in each pot one of the following weeds was sown:

Monocotyledons

15	Echinochloa crusgalli	(A)	15
	Avena fatua	(B)	
	Alopecurus myosuroides	(C)	
	Sorghum spp.	(D)	
	Setaria glauca	(E)	
20	Digitaria sanguinalis	(F)	20
	Panichum dichotomiflorum	(G)	
	Festuca pratensis	(H)	
	Bromus sterilis	(I)	
	Lolium italicum	(J)	
25	Dactylis glomerata	(K)	25

Dicotyledons

	Stellaria media	(L)	
	Ipomea purpurea	(M)	
	Vigna sinensis	(N)	
30	Convolvulus sepium	(O)	30
	Solanum nigrum	(P)	
	Amaranthus retroflexus	(Q)	
	Chenopodium album	(R)	
	Rumex acetosella	(S)	
35	Veronica persica	(T)	35

Water in an amount as required to ensure good germination of the seeds was added to each pot. The pots were divided into three sets.

The first set was not treated with any weedkillers and was used as a control.

The second set was treated one day after the sowing with a water-acetone dispersion (20% by 40 vol./vol.) of the compounds according to the invention, in order to evaluate the herbicide activity during pre-emergence.

The third set was treated 15 days after the sowing (i.e. when the plants, depending on the species, had already reached a height of 5 to 10 cm) with a water-acetone dispersion (20% by vol./vol.) of the compounds of the invention in order to evaluate the herbicide activity during post-emergence.

- All the pots were kept under observation in a condition environment at temperatures ranging from
 5 15 to 24°C, relative humidity = 70%, photoperiod = 12 hours, luminous intensity = 2000 lux.
 Every two days all the pots were uniformly sprinkled with water, taking care of wetting on the earth, so as to ensure a humidity degree sufficient for a good development of the plants.
 10 28 days after the treatment, the vegetative stage of the plants was determined and the corresponding evaluations were expressed according to a scale of values from 0 (growth equal to that of control) to 4 (complete stop of the growth or death of the plant). The results obtained are recorded in Tables 2 and 3.

5

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TABLE 2
 Herbicide activity during pre-emergence at the indicated doses

Compound No.	Dose of active substance (kg/ha)	Weeds									
		A	C	D	E	F	H	I	J	M	N
2	6									3	
8	6									4	3
9	6									4	
10	6									4	
30	2	3	4	3	3	4	4	3	3		

TABLE 3
Herbicide activity during post-emergence at the indicated doses

Compound No.	Dose of active substance (kg/ha)	Weeds																		
		A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
1	6												2	4	4	4	4	4	4	
	1												3	4	4	4	4	4	4	
2	6												3	3	4	4	4	4	4	
	1												3	3	4	4	4	4	4	
4	6												4	4	4	4	2	4	4	
	1												3	3	4	4	4	4	4	
6	6												3	4	4	4	3	3	3	
	1												3	3	4	4	3	3	3	
8	6												4	4	4	4	3	3	3	
	1												4	4	4	4	2	4	4	
9	6												4	4	4	4	3	3	3	
	2												4	4	4	4	3	3	3	
10	6												4	4	4	4	3	3	3	
	2												3	4	4	4	3	3	3	
18	6												3	4	4	4	3	3	3	
	2												3	4	4	4	3	3	3	
28	2												4	4	4	4	3	3	3	
	6												4	4	4	4	3	3	3	
30	6												4	4	4	4	4	4	4	
	2												4	4	4	4	3	3	3	

EXAMPLE 6

Selectivity towards useful cultures during post-emergence

Compounds of the invention were tested to determine their phyto-toxicity towards agrarian cultures.

- 5 Adopting the procedures described in Example 5 for the treatment during post-emergence, the damage due to the phyto-toxicity was evaluated on the following useful plants:

Wheat	(A')	
Beet	(B')	
Cucumber	(C')	
10 Parsley	(D')	10
Celery	(E')	
Fennel	(F')	
Bean	(G')	
Tomato	(H')	
15 Carrot	(I')	15

The damage due to the phyto-toxicity were expressed by means of the same scale of values as used in Example 5 for the herbicide activity, with indexes ranging from 0 (growth like that of the control) to 4 (complete stop of the growth or death of the plant). The results obtained are recorded on the following Table 4.

TABLE 4
Phyto-toxicity on useful cultures at the indicated doses

Compound No.	'Dose of active substance t(kg/ha)	Useful plant								
		A'	B'	C'	D'	E'	F'	G'	H'	I'
28	4	0	0		0	0	0			0
30	4	1	0	1				0	1	

EXAMPLE 7

Setting test on tomato

Tomato plants cv. Marmande, grown in a glasshouse at a temperature of 18 to 21°C, were transplanted into pots having a diameter of 35 cm. During the growth of the plants the side-shoots were continuously eliminated in order to have plants with only a central stem.

- 25 When the first flower axil exhibit 3 to 4 flowers on the anthesis, it was sprayed with a water-acetone solution (20% by volume of acetone) containing a wetting agent and the products being tested at a concentration of 100 ppm.

The treatment was repeated after 7 days.

- 30 Twelve days after the second treatment the fruits were picked and weighed.
For the purposes of a control, a set of tomato plants was cultivated in a similar manner and was treated only with a water-acetone solution without any phyto-growth regulator.

The results of the test, expressed as average weight of the fruits, are reported in the following Table 5.

TABLE 5
Setting of tomato flowers

Compound No.	Average weight of the fruits (g)
1	40.42
2	52.86
9	48.02
18	41.87
23	50.19
26	41.53
β -NOA ⁽¹⁾	45.37
Control	17.68 ⁽²⁾

(1) β -NOA = β -naphthoxyacetic acid, commercial phyto-growth regulator.

(2) 17.68 g = average weight of the fruits of plants not treated with phytogrowth regulators.

These results unequivocally prove that products of general formula (I) are endowed with a setting activity.

Furthermore, their activity is comparable, or in some cases superior to the one of β -naphthoxyacetic acid, a commercially available phytogrowth regulator utilized for the setting of tomatoes in glasshouses. 5

EXAMPLE 8

Tests of drop-preventing activity

Apple plants cultivated in pots and grown in a glasshouse were sprayed with water-acetone dispersions (20% by volume of acetone) containing the product being tested at a concentration of 30 ppm. Three days after the treatment, 20 leaves for each tree were cut, leaving the stalks attached to the branches. 10

After a further 11 days from the treatment, the percentage of stalks which detached was evaluated by exerting a slight pressure with the hand. 15

For the purpose of a control, an analogous test was carried out on apple plants treated only with a water-acetone solution without any phytogrowth regulator.

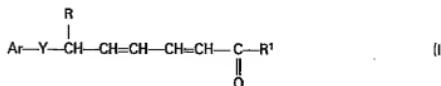
The results of the tests, expressed as a percentage of fallen stalks, are reported in the following Table 6.

TABLE 6
Drop-preventing activity on apple tree leaves

Compound No.	Percentage of fallen leaf stalks (%)
1	0
6	6.4
9	25.6
23	14.3
Control	67.5

CLAIMS

1. A compound of the general formula



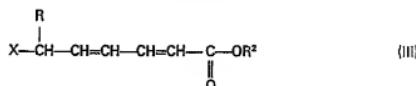
in which:

- 5 R represents a hydrogen atom or a methyl group,
Y represents an oxygen atom or a divalent sulphur atom,
R¹ represents OR², SR² or NR², in which R² represents a hydrogen atom, an alkyl group having 1 to 4 carbon atoms, a cycloalkyl group having 3 to 6 carbon atoms, an alkenyl group having 2 to 4 carbon atoms, an alkynyl group having 2 to 4 carbon atoms, a phenyl group or a benzyl group,
10 Ar represents a phenyl, pyridyl, naphthyl, quinoline, phenoxy-phenyl or a pyridyloxyl-phenyl group, any of which groups may be substituted by one or more substituents selected from halogen atoms, alkyl groups having 1 to 4 carbon atoms, alkoxy groups having 1 to 4 carbon atoms, nitro, cyano, trifluoromethyl, acetoxy, acetamido and methoxy carbonyl groups.
15 2. A compound as claimed in Claim 1, in which R¹ is an OR² and R² is a hydrogen atom or a methyl group.
16 3. A compound as claimed in Claim 1 having the structure of any one of compound Nos 1 to 33 in Table 1 herein.
17 4. A compound as claimed in Claim 1 substantially as herein described with reference to any one of Examples 2 to 8.
20 5. A process for preparing a compound as claimed in Claim 1, in which, R¹ is a group OR² and R² is a hydrogen atom or an alkyl group of 1 to 4 carbon atoms, in which an alkaline salt of formula



In which:

- M[⊕] represents the cation of an alkaline metal, and
25 Ar and Y are as defined in Claim 1,
is reacted in an inert gas atmosphere, in a polar solvent and at temperatures ranging from the room temperature to the solvent boiling temperature with an ester of formula



in which:

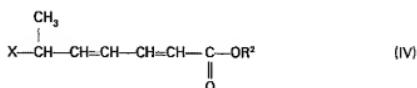
- 30 X represents chlorine, bromine or iodine atoms,
R an alkyl group having 1 to 4 carbon atoms, and
R represents a hydrogen atom or a methyl group, to yield compounds of formula (I) in which R² is an alkyl group having 1 to 4 carbon atoms and optionally hydrolysing said compounds to yield compounds of formula (II) in which R² is a hydrogen atom.
35 6. A process as claimed in Claim 1 substantially as herein described with reference to any of Examples 1 to 4.
7. A method of fighting infestations of mono- and di-cotyledons, during pre-emergence or post-emergence, consisting in distributing, in the area to be protected, an effective amount of one or more of the compounds as claimed in any one of Claims 1 to 4, either as such or in the form of a composition.
40 8. A method as claimed in Claim 7 in which, the effective amount is in the range 0.3 to 6 kg/ha.
9. A method as claimed in Claim 7, substantially as herein described with reference to Example 5.
10. A weed-killing composition containing, as an active substance, one or more of the compounds of Claim 1 in an amount of from 1 to 99% by weight.
45 11. A method of promoting the development and the rooting of useful plants or of increasing the fruit harvest, consisting in treating the plant or a part thereof with an effective amount of one or more of the compounds as claimed in any one of Claims 1 to 4 either as such or in the form of suitable compositions.
12. A method as claimed in Claim 11, comprising the setting treatment of tomato or pepper cultures in a glasshouse.
50 13. A method as claimed in Claim 12 in which, said compound(s) is applied in water at a concentration in the range 10 to 200 mg/l.

14. A method of Claim 11 comprising the drop-preventing treatment of the fruits before the harvesting.

15. A method as claimed in Claim 14 in which said compound(s) is applied in water at a concentration in the range from 1 to 10 g/l.

5 16. A phytogrowth regulating composition containing, as an active substance, one or more of the compounds as claimed in any one of Claims 1 to 4. 5

17. A compound of the general formula



in which:

10 X represents a chlorine, bromine or iodine atom, and
R² represents an alkyl group of 1 to 4 carbon atoms.

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